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Stochastic processes with a special class of non-stationary transition rates (NSTR) that can be related to stationary transition rates (STR) by time scale transformations are considered. Calculations are carried out on the time scale on which the process has STR and then related to the time scale of measurements by a time scale transformation. Application is made to Gaussian Markoff processes with a single transition rate. The resulting equilibrium autocorrelation function departs from weak stationarity.

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20. ABSTRACT *(Continued)*

A response function is related to the autocorrelation function and specialized to relaxation processes to yield a model consistent with Ngai's recent model of relaxation. The model is therefore widely applicable in the description of measured relaxation behavior and leads naturally to Ngai's renormalization relation for excitation energies. On the basis of the success of the model, consideration is given to the possibility that the process should be viewed as one with STR and an intrinsic time scale so that the process only appears to have NSTR on the time scale of measurements.

# CONTENTS

# RELAXATION PROCESSES AND TIME SCALE TRANSFORMATION

## I.  Introduction

This report is concerned with the study of processes with non-stationary transition rates (NSTR) all of which can be expressed as products of stationary transition rates (STR) and the same function of the experimentally-measured time. The latter function is so specified that the process can be viewed as one with STR on a different time scale. Then the original process with NSTR can be viewed as derivable from a process with STR by means of a time scale transformation. Despite the fact that the class of NSTR considered is thereby rather limited, the specification allows one to maintain the computational simplicity of processes with STR while investigating the prototypal effects of NSTR in the description of physical processes.

The concept of time scale transformations is already familiar from discussions of homogeneous and non-homogeneous Poisson processes,[1] has been mentioned as a possibility in discussions of the master equation,[2] and has recently been applied in cumulative damage models with discrete time parameter.[3] However, it does not seem to have been exploited generally in the description of relaxation processes. The object of this report is to consider relaxation processes in the context of time scale transformations in order to gain insight into the properties of relaxation processes with NSTR on the time scale of measurements.

The next section deals with the specification and nature of time scale transformations. In the third section, the phenomenology of the departure from weak stationarity (time translational invariance of autocorrelation functions) in the response of physical systems is discussed. In the fourth section, a time regime of relaxation is specified to be one in which there is a relaxation time for a NSTR process that is related to the relaxation time of the STR process by the same time scale transformation used to connect the respective processes. This leads to the requirement that the time scale transformation is monomial in the time regime of relaxation. The resulting model of relaxation processes will be referred to as the monomial relaxation

model and designated the MRM. It is noted that a widely applicable model of relaxation processes[4,5] is an important example of an MRM.

In the fifth section, it is emphasized that the customary model of relaxation that employs a weighted sum of weakly stationary autocorrelation functions (corresponding to a distribution of relaxation times) is not consistent with an MRM. It is also argued that the weighted sum model does not have a satisfactory physical basis, and therefore it is not a satisfactory model for relaxation processes.

A summary and discussion of the concepts and results of the report are presented in the final section.

## II. Time Scale Transformation and Transition Rates

A time scale or development parameter is taken to be a positive, cumulative function that increases from an origin monotonically. Consider two continuous time scales $\theta$ and $t$ where $\theta$ may be expressed as a function of the experimentally measured time $t$. Without loss of generality, $\theta$ and $t$ may be taken to be aligned such that their origins coincide.

$$\theta = \theta(t), \; \theta(0) = 0 \; . \tag{2.1}$$

Specify further that $d\theta/dt$ is positive, and finite everywhere except possibly at isolated points. The case of constant $d\theta/dt$ shall be excluded as uninteresting so that a simple linear transformation is not considered. The relationship between $\theta$ and $t$ is therefore essentially nonlinear.

Suppose now that transition rates on the $\theta$ time scale, $W(\theta)$ are stationary (constant). Then

$$W(\theta) = W_s \; . \tag{2.2}$$

On the $t$ scale, the transition rates

$$W(t) = W_s \, (d\theta/dt) \tag{2.3}$$

are non-stationary since $d\theta/dt$ is a non-trivial function of $t$. $W(t)$ is increased or decreased with respect to $W_s$ depending on the evolving magnitude of $d\theta/dt$. If $W$ represents a matrix of transition rates, the matrix is stationary on the $\theta$ scale and all components of the matrix are subjected to the same time scale transformations.

There are several points worth noting. Time scale transformations do not affect the order of events so causality is maintained. Also time scale transformations do not affect the mechanism of transitions but only the way the transitions are counted. Thus the properties of a process that depend on nature of the state space in which it takes place are unaffected. Hence a

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Markoff process remains a Markoff process and a nonMarkoff process remains a nonMarkoff process under time scale transformations. Finally, it should be emphasized that the concept of time scale transformations was introduced as an artifact to provide computational simplicity in the consideration of a class of NSTR. However, when physical processes are accurately describable in terms of this limited class of NSTR, one might also consider the processes actually to have STR and to be describable on an "intrinsic" time scale. Then the intrinsic time scale is related to the experimentally measured time scale by means of the time scale transformation.

## III. Departure from Weak Stationarity

It is useful now to consider the effects of NSTR (compatible with the time scale transformation formalism) in stochastic processes. It will be sufficient for present expository purposes to consider Gaussian Markoff processes with only a single, scalar transition rate. Again the starting point will be a description of the process on a time scale for which the transition rate is a constant.

Let $\alpha$ be a random variable representing deviations from equilibrium. Then the fluctuation process may be presented by a linear regression or Langevin-type equation

$$d\alpha/d\theta = - W_s \alpha(\theta) + \varepsilon(\theta) \tag{3.1}$$

Here the effective decay interaction is linear (i.e. $-W_s \alpha$) and it is assumed that $\varepsilon(\theta)$ is Gaussian with moments

$$\langle\varepsilon(\theta)\rangle = 0 \tag{3.2a}$$

$$\langle\varepsilon(\theta_2) \varepsilon(\theta_1)\rangle = 2\lambda\delta(\theta_1-\theta_2) \tag{3.2b}$$

The brackets $\langle\ \rangle$ represent stochastic averaging. It should be emphasized that it is assumed the correlations of the fluctuations are negligibly short on the $\theta$-scale so that the $\delta$-function is a functional of t. Although the introduction of the $\delta$-function (negligibly short correlations for the stochastic driving term) here is not formally correct,[6] its use in a straightforward way does lead to the same results as in rigorous development.[7]

One may also question the use of a differential stochastic equation on a more fundamental level.[8] Equation (3.1) is already irreversible so that it can only be valid after an "induction" period in which microscopic reversibility is suppressed. Moreover it is clearly phenomenological since it describes a system already decoupled from its environment with both reactive forces and fluctuation sources represented as effective interactions within the system.

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Nevertheless on the phenomenological level, such an equation may provide a satisfactory description of a physical process, at least in some time regime where reference is made to an apparent origin. Indeed the success of the usual Langevin equation on the t-scale bears witness to its usefulness.

Here the customary phenomenological description is generalized somewhat by considering Eq. (3.1) to be valid on the $\theta$ time scale. However, one would expect the $\theta$ and t scales to coincide at the very earliest times since the physical mechanisms that lead to NSTR must first be established before there is a difference between the two time scales. Similarly at very long times when regression is completed, time differences must coincide so that $d\theta/dt$ must become unity. It is in intermediate regimes that NSTR are present and lead to interesting physical effects.

As usual, the equilibrium distribution is taken to Gaussian and may be viewed as resulting from an expansion of the entropy with retention only of quadratic terms.[9]

$$P(\alpha) = (g/\pi k)^{\frac{1}{2}} \exp[-g\alpha^2/k], \tag{3.3}$$

where k is the Boltzmann constant. Also since the restoring force $X=\partial S/\partial\alpha=-g\alpha$, g is a linear force coefficient expressed in entropy units. It can be converted to energy units by multiplication by the absolute temperature, T.

The usual results for equilibrium fluctuations follow, e.g.

$$<\alpha(\theta)> = \alpha(0) \exp[-W_s\theta] \tag{3.4}$$

$$\{<\alpha(\theta)>\} = 0 \tag{3.5}$$

where $\{\ \}$ represents an average over the equilibrium distribution. Also from the requirement that the equilibrium distribution is independent of $\theta$, it follows that

$$\lambda = kW_s/g \tag{3.6}$$

Then the autocorrelation function takes the form

$$\{<\alpha(\theta)\alpha(0)>\} = kg^{-1} \exp[-W_s\theta] . \tag{3.7}$$

This autocorrelation function is invariant under positive translations of the origin of the $\theta$ time scale so the process is weakly stationary[10] on the $\theta$ time scale. However, when re-expressed in terms of t, the autocorrelation function is obviously not invariant for translations of the origin of t. Thus as physically measured, the process is not weakly stationary. The weak stationarity of the description on the $\theta$ time scale may be understood as a reflection of the arbitrariness in the alignment of the two time scales. However since the (apparent) origin of the experimentally measured time does enter in

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a non-trivial way for a nonweakly stationary process, it is reasonable to align the two origins as in Eq. (2.1). If this alignment is made, Eq. (3.7) no longer implies weak stationarity since translations of $\theta$ are no longer allowable operations.

Thus a direct consequence of introducing NSTR is the departure from weak stationarity. In a sense, the formalism is complementary to the more usual efforts to generalize weakly stationary Markoff processes to weakly stationary nonMarkoff processes that involve transformations in the state space. However the need for a departure from weak stationarity in the description of physical processes is a recurrent theme in the literature.[11,12,13] The time scale formalism used in this report provides a straightforward means of introducing such a departure while still retaining the computational simplicity associated with weakly stationary processes.

## IV. The Monomial Relaxation Model

Consider now the dynamics of a macroscopic perturbation $\bar{\alpha}$ caused by an external force $\bar{X}$ to be represented on the $\theta$ time scale by

$$d\bar{\alpha}/d\theta = L\bar{X} \quad . \tag{4.1}$$

Again a linear approximation is made for $\bar{X}$ when $\bar{\alpha}$ is undergoing decay, and it is assumed that the path of a decay is the same as that for a regression of a fluctuation $\alpha$ in section III. In energy units,

$$\bar{X} = -gT\bar{\alpha} \quad , \tag{4.2}$$

where $T$ is the absolute temperature. Then the following identity holds,

$$W_s \equiv LgT \tag{4.3}$$

It follows that

$$\bar{\alpha}(\theta) = (gT)^{-1} \exp[-W_s\theta] \, \bar{X}(0) \tag{4.4}$$

On the basis of Eq. (4.4), one may define a time dependent response function, $Z(\theta)$, as

$$Z(\theta) \equiv (gT)^{-1} \exp[-W_s\theta] \tag{4.5}$$

Then from Eq. (3.7), it follows that

$$Z(\theta) = (1/kT) \, \{<\alpha(\theta)\alpha(0)>\} \tag{4.6}$$

This formula for the response function may be immediately recognized as being of the Kubo-Green type[14] in the classical regime.

Given this general framework, it is now desirable to apply it to a problem of physical interest. First observe that the reciprocal of $W_s$ may be identified as a relaxation time $\tau_s$, and the response function Eq. (4.5) is dependent only on the ratio $\theta/\tau_s$. In other words, $\tau_s$ acts as a natural unit of time.

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Now define, in general, a relaxation process to be one for which the time dependence is controlled by a function only of the ratio of the time to a relaxation time $\tau$. This relaxation property does not in general hold on the $t$ time scale. However suppose there is a time regime for which the relaxation property holds on the $t$ scale and such that the $\theta$ and $t$ scales are aligned at the apparent origin. Moreover suppose there is a self-consistency in the definition of relaxation times so that they are related by the same time transformation that relates the two time scales, i.e.

$$\theta(\tau) = \tau_s \equiv W_s^{-1} \tag{4.7}$$

Then the negative of the argument of the exponential in Eq. (4.5) is a function of $t/\tau$, namely $f(t/\tau)$ and

$$f(t/\tau) = \theta(t)/\theta(\tau) \tag{4.8}$$

In order for Eq. (4.8) to be valid, $\theta(t)$ must be a monomial function, i.e.

$$\theta(t) = at^b \tag{4.9}$$

where $a$ has the dimensions of time to the $(1-b)$th power and $b>0$ so that $d\theta/dt$ is positive and $\theta$ satisfies Eq. (2.1). A system that is in the relaxation regime so that Eq. (4.9) holds, will be said to be described by a monomial relaxation model or MRM.

Recently, Ngai and coworkers[5,15-18,22,23] have described a whole host of physical relaxation phenomena with a model that can be cast in the form of an MRM. The appropriate time transformation is

$$\theta(t) = b^{-1}(e^\gamma \omega_c^0)^{b-1} t^b \quad , \quad 0<b<1 \quad , \tag{4.10}$$

where $\gamma$ is the Euler constant and $\omega_c^0$ is a cutoff frequency for low energy correlation excitations that are introduced to account for the statistical behavior of energy levels in a complex system. The existence of the cutoff frequency indicates that the process is being described for times greater than the reciprocal of the cutoff frequency. Also since $b$ is less than 1, the effect of the time transformation is to spread out a given number of transitions over increasingly lengthy time intervals. One may expect then an MRM of the Ngai type to describe physical phenomena that exhibit anomalous longtime or low frequency behavior.

The time dependence of the response function, namely $\exp[-(t/\tau)^b]$, which will be designated the monomial response function or MRF has often been used to fit relaxation data. Indeed Struik in a brief historical review[20] has noted its application for more than half a century to such diverse phenomena as stress relaxation in fibrous materials and glasses, volume recovery of

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inorganic glass quenched from above to below the glass transition temperature, stress relaxation and elastic recovery of unvulcanized rubbers, and the dielectric relaxation of many amorphous polymers. The wide applicability of the MRF has also been emphasized by Ngai[5,15-18] who has applied it in the analysis of measurements of dielectric response, mechanical response, nuclear spin-lattice relaxation and transient transport in materials of widely different chemical configurations and physical states. For example, Ngai and Henvis[17,21] have reviewed essentially all available dielectric susceptibility (relaxation) data with non-overlapping distinct peaks, and shown that the entire curves are consistent with a description in terms of the MRF with appropriate choices of $0 < b \leq 1$.

So far the discussion of the use of the MRF has referred to its application over an extended time period or equivalently an extended frequency range. However the $1/e$ value of the relaxation that occurs at $t = \tau (\theta = \tau_s)$ is an important indicator that is often measured either directly or by derivation from the placement of the peak of the imaginary part of the frequency dependent susceptibility. As Ngai[5] has emphasized the temperature dependence of such measurements is controlled by the temperature dependence of $\tau^b$ or equivalently $\tau_s$. Then if $E_A$ is the activation energy of $1/e$ value, the temperature of $\tau$ is controlled by an effective activation energy

$$E_A^* = E_A/b \quad , \quad 0 < b < 1 \tag{4.11}$$

Straightforward analysis of data provide a value for $E_A^*$. To obtain the true value of the activation energy, one should multiply $E_A^*$ by b. Thus $E_A^*$ will always appear greater than the true activation energy.

For example, Ngai[5,16] has analyzed dispersive transport data for the activation energy of small polaron hopping in $\alpha$-$SiO_2$ prepared by thermally oxidizing Si under different conditions such that independently determined values of b can be varied significantly. In such measurements, the transit time $t_\tau$ plays the role of the relaxation time in an MRM, and the b parameter can be determined from the shape of the current time dependence. Within experimental error, he found $E_A$ to be invariant, and to coincide closely with its value when directly measured in the very short time regime.[24] At temperatures lower than a third of the Debye temperature the small polaron mobility $\mu$ becomes non-Arrhenius, a well-known[24] signature of small polaron hopping. Since b is constant in this temperature regime, this non-Arrhenius behavior of log $\mu$ versus $1/T$ may be described in terms of a temperature dependent activa-

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tion energy of $E_A(T) \equiv \partial(\ln(1/\mu))/\partial(1/T)$. Then the measured temperature dependence of the transit time $t_\tau$ is controlled by the effective activation energy $E_A^*(T) \equiv \partial(\ln(t_\tau))/\partial(1/T)$ which is related to $E_A(T)$ by Eq. (4.11). It is remarkable that this relation is verified for the entire temperature range studied experimentally. Similarly, Ngai[5,17] and Taylor and Ngai[18] have analyzed transient hole transport measurements in $\alpha$-$As_2Se_3$ for undoped samples and samples doped with Cu, Tℓ, I, Ga, In, etc. In these samples the b values changed with doping. The measured $E_A^*$, the activation energy for the transit time, is a function of dopant and the doping level. In each case, Eq. (4.11) remained valid for a constant $E_A$ that corresponds to the small polaron mobility activation energy.

In other work, Starkweather and Barkley[19] carried out a controlled study of the dielectric relaxation of molecular group in nylon for which b was varied by varying environmental conditions (humidity). Again $E_A$ remained invariant in these measurements. The case of nylon with many molecular groups provides an interesting caveat to the present discussion. In cases when there are more than one distinct relaxation process involved as, for example, for the respective relaxations of different, separated molecular groups in a complex polymer, there is no reason to believe they would all share the same b parameter even if they were all in respective relaxation regimes of time. In the latter case, one would expect each process to be characterized by its own b or time scale transformation.

An additional facet of Eq. (4.11) may be observed when b is a function of temperature. Such a situation arises in inorganic glasses and amorphous polymers that have a glass transition. Here b as determined in dielectric or mechanical relaxation, or photon correlation spectroscopy measurements can be a function of temperature in a temperature region near or above the glass transition temperature where the materials undergo a glass-liquid or glass-rubber transition. From Eq. (4.11), $E_A^*$ would then also be temperature dependent so that the temperature dependence of the measured process would depart from Arrhenius behavior. This correlation between $E_A^*$ and b(T) has been quantitatively established[22] for some twenty polymers, for $B_2O_3$, for the molten salt 0.4 $Ca(NO_3)_2$ 0.6 $KNO_3$ and other materials.[23] For the cases of glasses and glassy polymers, Eq. (4.11) together with b as a function of temperature is equivalent to the Vogel-Beuche-Fulcher empirical law for viscosity[24] or the Williams-Landel-Ferry empirical law for viscoelastic and dielectric relaxations.[25,26]

Together the wide applicability of the MRF and the validity of the more subtle renormalization relation Eq. (4.11) provides considerable credibility for the MRM. This is perhaps surprising because the MRM is based on a special case of the limited class of NSTR that are compatible with time scale transformations. A possible way to understand this wide physical applicability is to consider that there is a general principle at work. Namely, once the phenomenological regime of a response process is reached, the process has STR but has its own intrinsic time which can be related to the measured time by a monomial function in the relaxation regime. The alignment of the origins of the $\theta$ and $t$ time scales reflects the fact that the process is initiated by events that are measured on the $t$ time scale. In other words, one could take time scale transformation as fundamental and the NSTR as the artifact.

## V. The MRM and Distribution of Relaxation Times

It has been demonstrated in the previous section that the MRM characterized by the monomial response function (MRF) provides a widely applicable description of relaxation phenomena. From another viewpoint the MRF is one of many possible examples of an empirical deviation of relaxation phenomena from simple Debye behavior.[27] From that viewpoint, the MRF is just an empirical result of the weighted sum of simple exponential response functions with different relaxation times. With the weighted sum in the form of an integral, one can write

$$\exp[-(t/\tau)^b] = \int_0^\infty d\tau' g(\tau') \exp[-(t/\tau')], \quad 0<b<1 \qquad (5.1)$$

where

$$\int_0^\infty d\tau' g(\tau') = 1 \ , \ g(\tau') \geqq 0 \quad . \qquad (5.2)$$

Here $g(\tau')$ is a real function with dimension of reciprocal time that represents the distribution of relaxation times.

One implication of Eq. (5.1) is that the individual response functions included in the integral are independent since the distribution of relaxation times is not introduced in the state space but only after the individual responses have been established. The numerical equivalence of the two sides of Eq. (5.1) would then have to result from the occurrence of an appropriate weighting of the simple exponential responses. However as emphasized in the previous section, the form of the MRF is so pervasive in nature that it would be a remarkable accident if physical weighting functions could so consistently result in an empirical expression that coincides with the MRF.

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In Eq. (5.1) the origins of the component response functions within the integral have been aligned and the integral is weakly stationary. As discussed in Section III, the left hand side is not. One could resolve this incompatibility by specifying that the weak stationarity of the right hand side is only apparent so that the origin in t is taken to be fixed. Such a requirement on the use of the weighted sum of simple exponential response functions is not typically noted and indeed the weak stationarity property is frequently employed. Thus the use of the weighted sum model can be misleading.

Moreover the concept of renormalization of the activation energies as in Eq. (4.11) becomes submerged when the left hand side is thought to be only an empirical artifact rather than a representation of true temporal behavior. For then, the temperature dependence of the relaxation time for the process is naturally identified with that of the average of the distributed relaxation times. Such an average is not characterized by the appropriate renormalized excitation energy. Indeed for the case b=½, $g(\tau')$ is known in a closed form,[28] viz.

$$g(\tau') = (4\pi\tau \; \tau')^{-\frac{1}{2}} \exp-(\tau'/4\tau) \qquad (5.3)$$

so that the average relaxation time (the integral of $\tau'$ weighted by $g(\tau')$ over all $\tau'$) is just

$$<\tau'> = (2)\tau \qquad (5.4)$$

This linear relation between $<\tau'>$ and $\tau$ shows that they both have the same temperature dependence and the concept of energy renormalization never arises.

Furthermore, the distribution of relaxation times is often attributed to "randomness" or "disorder." There are many relaxation processes such as the β relaxations in polymers that have a wide distribution of relaxation times and yet each of their temperature dependence is governed by a constant activation energy. It is difficult to understand why the "randomness" or "disorder" does not give rise to a distribution of activation energies which then would not have an Arrhenius behavior over extended temperature range.

To summarize, the weighted sum of simple exponentials can lead to an empirical form that coincides numerically with an MRF. However, the pervasiveness of the form of the MRF in a wide range of material types and physical states makes it difficult to understand why the weightings will always lead to that form. Further, the weighted sum model is at best misleading in its implication of weak stationarity. Finally, one of the most important properties of the MRF, namely the renormalization of the activation energy does not

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arise naturally in the weighted sum model. Thus given that the MRM leads to a MRF that characterizes a single correlated system, incorporates departure from weak stationarity in a direct way, and introduces renormalization of activation energies consistent with physical observations, one is led to choose the MRM as the model of choice here.

VI. Concluding Remarks

The effect of nonstationary transition rates (NSTR) in systems described on time scale of measurements has been studied for a limited class of NSTR that can be represented as stationary transition rates (STR) on a different time scale. Calculations have then been carried out for systems with STR and the ensuing results related to systems with NSTR by means of a time scale transformation. The time scale transformation is then a convenient artifact that allows one to maintain computational simplicity.

A particular physically realistic result is the derivation of equilibrium autocorrelation functions that are not weakly stationary. Also the formalism is used to develop a model of relaxation phenomena, the monomial relaxation model (MRM), that is applicable in the description of most measurements of relaxation phenomena. The MRM is consistent with Ngai's recent model so that, as in that model, there is a natural renormalization of activation energies that is verified by empirical results.

The success of the MRM leads one to consider that it may be the result of a general principle rather than just based on a special case of the limited class of NSTR initially considered. Namely, it may be that the phenomenlogical description of many response phenomena involve processes that have STR and are characterized by an intrinsic time scale. Then the time scale transformation is an essential operation that allows the process to be described on the time scale of measurement where the process appears to have NSTR. In that way, the NSTR become the artifacts and computational simplicity is a true characteristic of the process.

Whatever viewpoint is taken, the present treatment of NSTR on the time scale of measurements has already been used to provide a prototypal generalization of stationary Markoff processes, and to develop a widely applicable phenomeno-logical model of relaxation processes.

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